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SURFACE-ACTIVE AND FUNCTIONAL PROPERTIES OF CARBOXYMETHYL STARCH OCTENYL-SUCCINATES

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ABSTRACT: Carboxymethyl starch octenyl-succinates (OS-CMS) were prepared in dimethylsulfoxide/p-toluenesulfonic acid (DMSO/pTSA) system under classical and microwave heating. Derivatives were characterised by FT-IR spectroscopy. The critical micelle concentration and corresponding maximal lowering of surface tension of derivatives solutions in water and 0.5 M NaCl were assessed. Surface saturation, minimal area per molecule and further thermodynamic parameters were calculated making evidence, that addition of salt had positive effect on adsorption of molecules at the surface. Octenylsuccinylation leaded to enhanced emulsifying efficiency giving emulsions stable for several hours comparable with commercial standard Tween 20.

KEY WORDS: octenylsuccinates of carboxymethyl starch, esterification, surface-active properties, microwaves

1. INTRODUCTION

Carboxymehyl starch (CMS) as a commercially available polysaccharide provides a wide range of applications. It is commonly used in food, paper, textile and pharmaceutical industry [1]. Further modification introducing hydrophobic side groups into hydrophilic CMS backbone leads to water-soluble amphiphilic derivatives, which are able to absorb on the interface [2,3]. Octenyl-succinic anhydride (OSA) has been dealt in various research works [4-8] as an appropriate modification agent for preparation of amphiphilic derivatives due to its dual hydrophobic and hydrophilic character. Moreover, desirable changes in solution properties and viscosity have been observed [9].

The modification of starch with octenyl-succinic andydride was patented by Caldwell and Wurzburg (1953). The esterification was performed in aqueous slurry medium under mild alkaline conditions [10]. Low DS starch succinates could be also obtained by refluxing in pyridine in the presence of succinic anhydride with or without prior gelatization of starch by heating in 60 % aqueous pyridine and subsequent distilling the pyridine water azeotrope from the mixture and replacing it with 100 % pyridine [11, 12]. Another method is based on esterification of starch in dimethylacetamide/LiCl system using pyridine as a catalyst [13].

In present work, we have concerned with preparation of carboxymethyl starch octenyl-succinates (OS-CMS) in dimethylsulfoxide/p-toluenesulfonic acid (DMSO/pTSA) system according to Vogt et al. (1996) [14], which was presented as a non-derivating solvent system for carboxymethyl cellulose. Surface-active properties of prepared derivatives have been studied and comparison between classical and microwave heating applied was performed.

2. MATERIALS

The carboxymethylated cold-water-soluble potato starch EMSIZE CMS 60 with 28 % amylose content, 11.2 % moisture content and degree of carboxymethylation (DS_{CM}) 0.1 was purchased from Emsland-Staerke GmbH (Emlichheim, Germany). Octenyl-succinic anhydride (OSA) of 97 % purity was purchased from Sigma-Aldrich Chemie GmbH (Munich, Germany). All solvents were of reagent grade and were used without further purification.

3. METHODS

3.1 Esterification of CMS

To a stirred suspension of 2 g (11.76 mmol) CMS in 25 ml of DMSO, 0.22 g pTSA (0.1 mol per mol CMS) was added at 60 °C and stirring was continued for ca. 90 min. The gel-like solution obtained was used in chemical modification without any additional treatment. Then, appropriate amount of OSA was added slowly during 1 h and the reaction was allowed to proceed for total 24 h at 60 °C. The product was precipitated with acetone, filtered, washed three times with acetone, and vacuum-dried at 60 °C for 24 h before testing.

Similarly, suspension of CMS in 10 ml of DMSO was pre-heated during 1 min in modified domestic microwave oven Sencor SMW 2220 at 140 W while stirring. Then, pTSA was added and another minute of microwave irradiation was applied. To a gel-like solution obtained, appropriate amount of OSA was added and the reaction was allowed to proceed for 1, 3 or 5 min of microwave irradiation (5 min of stirring between each minute of irradiation). The product was precipitated with acetone, filtered, washed three times, purified for 8 h by Soxhlet extraction with acetone and air-dried before testing.

3.2 Characterization of prepared OS-CMS derivatives

Prepared OS-CMS derivatives were characterized by means of FT-IR. Spectra were recorded on a Nicolet Magna 750 spectrometer using 128 scans at a resolution of 4 cm^{-1} in KBr pellets.

The surface tension of the polysaccharide solution in water and 0.5 M NaCl was determined in the concentration range between 0.015 and 5 kg/m^3 at 25 °C using the Du Noüy ring method.

Oil-in-water emulsions were prepared by mixing of 50 mg of sample dissolved in 9 ml of distilled water and 1 ml of paraffin oil dyed with Sudan IV. The laboratory mixer Heidolph DIAX 600 at 22 500 rpm was used.

4. RESULTS AND DISCUSSION

In order to find most appropriate way for preparation of OS-CMS water-soluble derivatives, the esterification of CMS with OSA was performed under various reaction conditions (Tab. 1).

Tab. 1: Results of esterification of carboxymethylstarch (CMS, DS_{CM} 0.1) with octenylsuccinic anhydride (OSA) at various reaction conditions.

		Reaction conditions			
		Heating	Temp. (°C)	Time	
AC-20	1:0.07	CH	60	24 h	0.89
AC-32/2	1:0.07	MW	79-120	5 min	0.76
AC-33/1	1:0.07	MW	80-100	3 min	0.83
AC-34	1:0.07	MW	90	1 min	0.82
AC-35*	1:0.07	MW	89-107	5 min	0.77

*24 h swelling in DMSO without pTSA, CH – classical heating, MW – microwave heating

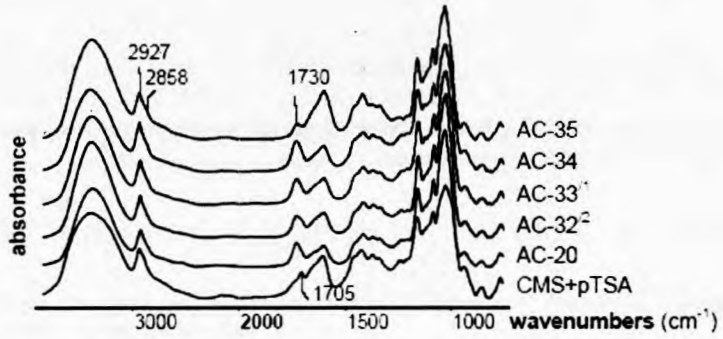

Fig. 1: FT-IR spectra of prepared OS-CMS derivatives and initial CMS pre-treated with pTSA.

The introduction of the octenylsuccinate (OS) groups can be evidenced by means of FT-IR spectroscopy (Fig. 1). The initial CMS pre-treated with pTSA contains carboxymethyl groups, which are partially protonated, giving a very weak νC=O band at ~1735 cm^{-1} (COOH) and a strong band of the carboxylate group (COO^-) at 1604 cm^{-1}. A weak band at 1705 cm^{-1} could be assigned to free acid formed during pre-treatment. The spectra of the obtained derivatives show an intense band at 1730 cm^{-1}, corresponding to the νC=O stretch of the esterified and free carboxyl groups (COOH) present in the OS substituent. The absence of bands at 1850 and 1780 cm^{-1} confirms that the products are free of the unreacted OSAs. As seen in spectra, extension of microwave irradiation time from 1 to 5 min did not have significant influence on degree of esterification giving comparable intensities of νC=O stretch bands at 1730 cm^{-1}. In order to avoid usage of pTSA, CMS was swelled during 24 h prior esterification (AC-35). The spectra shows less intense band at 1730 cm^{-1} due to the absence of contribution of νC=O stretches assigned to protonated carboxymethyl groups.

The critical micelle concentration (cmc) and the corresponding maximal lowering of surface tension (γ_{min}) of derivatives solution in water and 0.5 M NaCl were assessed from the concentration dependence of surface tension (γ). The efficiency (i.e. concentration at which the surface tension has reached a value half-way between the solvent value and the value at the cmc; $c_{1/2}$) and effectiveness (i.e. surface pressure defined as a difference of surface tension of pure water and γ_{min}; π_{cmc}) of the polymeric surfactant molecule was calculated according to [15].

Tab. 2: Critical micelle concentration (cmc), maximal lowering of surface tension (γ_{min}), efficiency ($c_{1/2}$) and effectiveness (π_{cmc}) of prepared OS-CMSs in water and 0.5 M NaCl.

	cmc (kg/m³)		γ_{min} (mN/m)		$c_{1/2}$ (kg/m³)		π_{cmc} (mN/m)	
	water	NaCl	water	NaCl	water	NaCl	water	NaCl
CMS	-	-	55.30	-	2.26	-	17.50	-
AC-20	-	-	63.98	-	1.95	-	8.82	-
AC-32/2	2.77	1.03	59.49	57.80	0.75	0.32	13.31	15.00
AC-33/1	2.50	1.92	56.26	50.80	0.04	0.01	16.54	22.00
AC-34	8.71	5.21	52.27	51.83	0.98	0.60	20.53	20.97
AC-35	1.48	1.25	67.20	55.70	0.43	0.15	5.60	17.10

As shown in Tab. 2, all OS-CMS derivatives lower surface tension only moderately, similarly to unmodified CMS. However, their surface activity was enhanced in the presence of 0.5 M NaCl solution, which modifies the inter/intramolecular force balance. Electrostatic repulsions between polymer charges are screened by salt ions resulting in polymer shrinking by dehydratation. This leads to formation of smaller polymer coils, which was confirmed by reducing of minimal area per molecule (A_{min}), shown in Tab. 3, calculated from relation:

$$A_{min} = 1/N_A \Gamma_{max} \quad (1)$$

where N_A is the Avogadro's number and Γ_{max} is the surface saturation of the polymeric surfactant at air/water interface. Γ_{max} was calculated using Gibb's adsorption equation for dilute systems:

$$\Gamma_{max} = -1/RT \times d\gamma/d \ln c \quad (2)$$

where R is the universal gas constant, T is the absolute temperature and $d\gamma/d \ln c$ is a slope of the $\gamma - \ln c$ dependence [16].

Tab. 3: The surface saturation (Γ_{max}), minimum area per molecule (A_{min}), Gibb's free energy of micellization ($\Delta G°_{mic}$), adsorption ($\Delta G°_{ad}$) and effective energy ($\Delta G°_{eff}$) of prepared OS-CMSs in water and 0.5 M NaCl.

	Γ_{max}		A_{min} (Å^2)		$-\Delta G°_{mic}$		$-\Delta G°_{ad}$ (kJ/mol)		$\Delta G°_{eff}$ (kJ/mol)	
	water	**NaCl**	**water**	**NaCl**	**water**	**NaCl**	**water**	**NaCl**	**water**	**NaCl**
CMS	4.44	-	37.41	-	-	-	-	-	-	-
AC-20	1.87	-	88.78	-	-	-	-	-	-	-
AC-32/2	2.11	2.60	78.85	63.86	10.32	12.73	16.64	18.50	6.32	5.77
AC-33/1	0.82	0.91	202.11	183.12	10.57	11.22	30.70	35.48	20.13	24.26
AC-34	1.99	2.00	83.52	83.00	7.68	8.78	18.01	19.26	10.33	10.48
AC-35	0.93	1.63	178.42	101.76	11.85	12.25	17.87	22.73	6.02	10.48

The Gibb's free energy of micellization ($\Delta G°_{mic}$) and adsorption ($\Delta G°_{ad}$) was calculated using Eq. (3) and Eq. (4), respectively [17]:

$$\Delta G°_{mic} = RT \ln cmc \quad (3)$$

$$\Delta G°_{ad} = \Delta G°_{mic} - \pi_{cmc}/\Gamma_{max} \quad (4)$$

More negative values of $\Delta G°_{ad}$ than their corresponding $\Delta G°_{mic}$ indicate that the adsorption of derivatives is favoured over micellization. The addition of salt enhanced the adsorption primarily (except of AC-32/2) giving greater decrease in $G°_{ad}$ than in $\Delta G°_{mic}$. This is evident from increasing values of effective Gibb's free energy ($\Delta G°_{eff}$) defined as a difference between $\Delta G°_{mic}$ and $\Delta G°_{ad}$.

The stability of the emulsion was observed during 24 h measuring the height (mm) of the oil and cream layer formed at the top of the emulsion. By most samples, the delay was evident before creaming begun. The delay was quantified by extrapolation of the cream layer height to zero movement, similarly to [18]. Moreover, the heights of the oil and cream layers formed after 5 min (h_1), 1 h (h_2) and 24 h (h_3) were recorded (Tab. 4). It is evident, that octenylsuccinylation leads to enhanced emulsifying efficiency giving emulsions stable for several hours comparable with commercial standard Tween 20.

Tab. 4: Emulsifying efficiency of prepared OS-CMSs

Sample No.		**Oil/Cream (mm/mm)**		
		h_1	h_2	h_3
CMS	0.05	0/3	0/8[b]	0/8[b]
AC-20	6.22	0/0	0/0	0/10
AC-32/2	1.22	0/0[c]	0/0[c]	0/1[c]
AC-33/1	-	0/0[c]	0/0[c]	0/0[c]
AC-34	1.02	0/0	0/0	0/8

AC-35	2.88	0/0	0/0	0/5
Tween 20	0.97	0/0	0/0	0/11

[a] time at which the height of cream layer exceeded the limit of 0.1 mm;
[b] oil drops dispersed in cream layer; [c] oil-rich foam formation

5. CONCLUSION

Octenylsuccinylation of CMS leads to derivatives with enhanced surface-active end emulsifying properties. Using of microwave irradiation instead of classical heating did not have a significant effect on degree of esterification. However, efficiency of prepared surfactants were enhanced. Addition of salt had positive effect on adsorption of molecules at the surface. Emulsifying efficiency of OS-CMS prepared under microwave irradiation was slightly lower, compared with the derivative prepared by classical heating, which may be caused by the drop in viscosity due to the degradation induced by microwaves. Further study should be made to evaluate the functional properties of OS-CMS derivatives and possibility to use them in textile laundry processing.

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